# This Page Is Inserted by IFW Operations and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

## IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents will not correct images, please do not report the images to the Image Problem Mailbox.

v	≅ <u> </u>				F11.1					1 Tal.		***
												j
				-								
												į
				, ·	100 K 100 K	•						*
					2"							
						·						
								· .	-			
		<b>5</b> ,					4 3 4					
	*											
			. •		Ag					a ·		
					100				1+	*		
			<b>1</b> .		e i North Anna (1997). E i North Anna (1997)							
										ŧ		
	<b></b> • • • • • • • • • • • • • • • • • • •											
											*	
												.3-
			~ .				1. J. A.			7		·
					* .				per			
									* .			
· ·	į. Į jas				100							
					v V					1		
								*				
, Z				© - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1			:	*				
, J							ing service of the se					
					. *****							
					. *****							
					. *****							
					. *****							
					. *****							
					. *****							
					. *****							
					. *****							
					. *****							
					. *****							
					. *****							
					. *****							
					. *****							
					. *****							
					. *****							

## PCI

## WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



### INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5: A61K 7/50, 7/48	A2	1) International Publication Number: WO 94/03152
Auta 7/30, 7/40		13) International Publication Date: 17 February 1994 (17.02.94
(21) International Application Number: PCT/EP (22) International Filing Date: 3 August 1993		vision, Colworth House, Sharnbrook, Bedford MK4
(30) Priority data: 9216758.4 7 August 1992 (07.08.92)  (71) Applicant (for AU BB CA GB IE LK MN MW NZ UNILEVER PLC [GB/GB]; Unilever House, ars, London EC4P 4BQ (GB).	SD on	LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU SD, SE, SK, UA, VN, European patent (AT, BE, CH DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT
<ul> <li>(71) Applicant (for all designated States except AU BB of LK MN MW NZ SD): UNILEVER NV [NL/NI 455, NL-3013 AL Rotterdam (NL).</li> <li>(72) Inventor: HELLIWELL, John, Fielden; 9 Cross Heswall, Wirral, Merseyside L60 9JA (GB).</li> </ul>	L]; Wee	Published  Without international search report and to be republished upon receipt of that report.

#### (54) Title: DETERGENT COMPOSITION

#### (57) Abstract

The invention relates to detergent compositions in liquid or gel form. The compositions comprise 5-50 %wt by weight of a non-soap detergent, which is preferably a mixture of a betaine and at least one of SLES and isetionate, 0.01-15 %wt of a cationic polymer and 0.5-15 % of a silicone. The compositions are characterised by a rod-micellar structure which provides a viscosity of at least 6000 centipoise at a shear rate of 10/sec. This rod-micellar structure can be generated by the presence of electrolyte or perfume in the compositions.

## FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

Austria Australia Barbados Belgium Burkina Faso Bulgaria Benin Brazil Belarus Canada Central African Republic Congo	FR GA GB GN GR HU IE IT JP KP	France Gabon United Kingdom Guinea Greece Hungary Ireland Italy Japan Democratic People's Republic of Korea Republic of Korea	MR MW NE NL NO NZ PL PT RO RU SD SE	Mauritania Malawi Niger Netherlands Norway New Zealand Poland Portugal Romania Russian Federation Sudan Sweden
				Slovak Republic
Cameroon China Czechoslovakia Czech Republic Germany Denmark Spain	LK LU LY MC MG ML MN	Sri Lanka Luxembourg Latvia Monaco Madagascar Mali Mongolia	SN TD TG UA US UZ VN	Senegal Chad Togo Ukraine United States of America Uzbekistan Vict Nam
	Australia Barbados Belgium Burkina Faso Bulgaria Benin Brazil Belarus Canada Central African Republic Congo Switzerland Côte d'Ivoire Cameroon China Czechoslovakia Czech Republic Germany Denmark	Australia GA Barbados GB Belgium GN Burkina Faso GR Bulgaria HU Benin IE Brazil IT Belarus JP Canada KP Central African Republic Congo KR Switzerland KZ Côte d'Ivoire LI Cameroon LK China LU Czechoślowakia LV Czech Republic MC Germany MC Denmark ML Spain MN	Australia GA Gabon Barbados GB United Kingdom Belgium GN Guinea Burkina Faso GR Greece Bulgaria HU Hungary Benin IE Ireland Brazil IT Italy Belarus JP Japan Canada KP Democratic People's Republic of Korea Central African Republic Congo KR Republic of Korea Switzerland KZ Kazakhstan Côte d'Ivoire LL Liechtenstein Cameroon LK Sri Lanka China LU Luxembourg Czechoślowakia LV Latvia Czech Republic MC Monaco Germany MG Madagascar Denmark ML Mali Spain MN Mongolia	Australia GA Gabon MW Barbados GB United Kingdom NE Belgium GN Guinea NL Burkina Faso GR Greece NO Bulgaria HU Hungary NZ Benin IE Ireland PL Brazil IT Italy PT Brazil IT Italy PT Brazil JP Japan RO Canada KP Democratic People's Republic RU Central African Republic of Korea SD Switzerland KZ Kazakhstan SI Côte d'Ivoire LI Liechtenstein SK Cameroon LK Sri Lanka SN China LU Luxembourg TD Czechoslovakia LV Latvia TG Czech Republic MC Monaco UA Germany MG Madagascar US Spain MN Mongolia

10

25

30

35

- 1 -

#### DETERGENT COMPOSITION

This invention relates to detergent compositions in liquid or gel form suitable for personal washing and having a specified minimum viscosity.

There are a variety of commercially available detergent products in liquid form which are intended for personal washing. Shampoos intended for hair washing are customarily formulated so as to have a viscosity which does not substantially exceed 5,000 centipoise at a shear rate of 10 sec<sup>-1</sup>. This enables such compositions to be worked into the hair of the user without undue difficulty.

By contrast some products intended for washing skin are formulated with a rather higher viscosity so that they will not run off too quickly when applied to the skin of the user. Shower gels are a typical form of detergent product frequently formulated to have relatively high viscosity.

It is known to include silicone in shampoo compositions as a hair conditioning aid. A difficulty however is that the emulsified droplets of silicone oil tend to come out of suspension and form a separate layer at the top of the liquid phase. It is known to include cationic polymer in shampoo compositions together with the silicone oil. The cationic polymer acts as another conditioning aid.

Nevertheless in order to obtain a shampoo composition which is stable on storage some additional measure is necessary. One possibility is to include a diester of a dihydric alcohol such as ethyleneglycol distearate which functions to structure the emulsion and inhibit the separation of silicone oil. Another approach is to incorporate compounds which are secondary alcohols having 2 alkyl chains extending from a central moiety which

- 2 -

includes the secondary hydroxyl group. These secondary alcohols and the diesters can be classified as compounds which incorporate 2 alkyl groups with a total of at least 20 carbon atoms between them. Other materials which have been proposed for this purpose are acyl derivatives in which the acyl groups contain at least 16 carbon atoms, amine oxide with alkyl chains of at least 16 carbon atoms, and Scleroglucan gums.

Specific compositions of the general type described above are found in EP-A-432951 (Unilever:1989). EP-A-432951 describes shampoo formulations comprising sodium lauryl ether sulphate and betaine surfactants, Jaguar cationic polymer and a silicone conditioner.

15

20

. 25

5

We have now found that when a detergent composition containing silicone and cationic polymer is formulated with a higher viscosity than is customary for a shampoo, the storage stability improves very remarkably and effectively ceases to be a problem. This is especially true when the average droplet size of the silicone is less than 2 μm in diameter. Therefore, according to the present invention there is provided a detergent composition in the form of an aqueous liquid or gel, a substantial part of which is in the rod-miscellar phase, containing

- 5 to 50% by weight of non-soap detergent,
- 0.01 to 5% by weight of cationic polymer, and
- 0.5 to 15% by weight of silicone,

30

where the detergent composition has a viscosity of at least 6,000 centipoise at a shear rate of 10  $\sec^{-1}$ . Preferably the viscosity is at least 7,000 centipoise at  $10 \sec^{-1}$  shear rate.

While it might be considered that a high viscosity product such as a shower gel would show a reduced tendency to

10

15

20

- 3 -

cream. We have observed that the addition of non-silicone oils to conventional shower gel formulations results in a destruction of the rod-micells and consequently to creaming of the added oil. Surprisingly, this does not occur where the oil is a silicone.

In this invention it is not necessary to include such structuring compounds as esters and alcohols having two alkyl or acyl groups with more than 20 carbon atoms in total, acyl derivatives in which the acyl groups each contain at least 16 carbon atoms, Scleroglucan gums and amine oxides incorporating alkyl groups with at least 16 carbon atoms. Such compounds are then preferably absent or if present, are included in an amount less than 0.5%.

The total amount of detergent in the composition preferably does not exceed 25% by weight, and may well not exceed 20% by weight. The amount of detergent may well be at least 8% or even at least 10% of the composition.

The detergent may be a variety of materials from the well known classes of non-soap anionic, nonionic, amphoteric and zwitterionic surfactants.

25 Preferably the detergent comprises anionic detergent either alone or accompanied by a zwitterionic detergent, for instance the anionic detergent may be 30 to 100%, preferably at least 50%, preferably not over 80% of the detergent present while the zwitterionic detergent is 0 to 70%, preferably at least 20%, preferably not over 50% of the detergent present.

One preferred anionic detergent is fatty acyl isethionate of formula:

 $RCO_2CH_2CH_2SO_3M$ 

20

- 4

where R is an alkyl or alkenyl group of 7 to 21 carbon atoms and M is a solubilising cation such as sodium, potassium, ammonium or substituted ammonium. Preferably at least three quarters of the RCO groups have 12 to 18 carbon atoms and may be derived from coconut.

Another preferred anionic detergent is alkyl ether sulphate of formula:

## ${\rm RO}\left({\rm CH_2CH_2O}\right){\rm _nSO_3M}$

where R is an alkyl group of 8 to 22 carbon atoms, n ranges from 0.5 to 10 especially 1.5 to 8, and M is a solubilising cation as before.

Other possible anionic detergents include alkyl glyceryl

ether sulphate, sulphosuccinates, taurates, sarcosinates,

sulphoacetates, alkyl phosphates and acyl lactates.

Sulphosuccinates may be monoalkyl sulphosuccinates having

the formula:

 $R^5O_2CCH_2CH(SO_3M)CO_2M$ ; and amido-MEA sulphosuccinates of the formula:  $R^5CONHCH_2CH_2O_2CCH_2CH(SO_3M)CO_2M$ ; wherein  $R^5$  ranges from  $C_8-C_{20}$  alkyl, preferably  $C_{12}-C_{15}$  alkyl and M is a solubilising cation.

Sarcosinates are generally indicated by the formula:  $R^5CON(CH_3)CH_2CO_2M, \text{ wherein R ranges from } C_8-C_{20} \text{ alkyl}, \\ \text{preferably } C_{12}-C_{15} \text{ alkyl and M is a solubilising cation.}$ 

Taurates are generally identified by the formula:  $R^5CONR^6CH_2CH_2SO_3M, \ wherein \ R^5 \ ranges \ from \ C_8-C_{20} \ alkyl,$  preferably  $C_{12}-C_{15}$  alkyl,  $R^6$  ranges from  $C_1-C_4$  alkyl, and M is a solubilising cation.

The anionic detergent included in the composition will generally be selected to avoid harsh detergent such as primary alkane sulphonate or alkyl benzene sulphonate.

30

35

15

25

30

- 5 -

The amount, if any, of these is preferably less than 3% of the detergents present.

Suitable zwitterionic detergents have a hydrophilic head group which contains both a quaternary nitrogen atom and at least one acid group which may be a carboxylic or a sulphonic acid group. Such detergents should generally include an alkyl or alkenyl group of 7 to 18 carbon atoms. They will usually comply with an overall structural formula.

10 formula

O
$$R^{1} - \left[-C - NH \left(CH_{2}\right)_{m} - \right] - N^{*} - X - Y$$

$$R^{3}$$

where  $R^1$  is alkyl or alkenyl of 7 to 18 carbon atoms  $R^2$  and  $R^3$  are each independently alkyl, hydroxyalkyl or carboxyalkyl of 1 to 3 carbon atoms

m is 2 to 4

n is 0 or 1

X is alkylene of 1 to 3 carbon atoms optionally substituted with hydroxyl, and

Zwitterionic detergents within the above general formula include simple betaines of formula:

$$R^{1}$$
 $R^{1}$ 
 $CH_{2}CO_{2}$ 
 $R^{3}$ 

35 and amido betaines of formula:

$$R^{1} - CONH(CH_{2})_{m} - N^{*} - CH_{2}CO_{2} - \frac{1}{R^{3}}$$

- 6 -

where m is 2 or 3.

In both formulae  $R^1$ ,  $R^2$  and  $R^3$  are as defined previously.  $R^1$  may in particular be a mixture of  $C_{12}$  and  $C_{14}$  alkyl groups derived from coconut so that at least half, preferably at least three quarters of the groups  $R^1$  have 10 to 14 carbon atoms.  $R^2$  and  $R^3$  are preferably methyl.

A further possibility is that the zwitterionic detergent is a sulphobetaine of formula:

$$R^{2}$$
|
 $R^{1}-N^{*}-(CH_{2})_{3}SO_{3}^{-}$ 
|
 $R^{3}$ 

or

$$R^{1}$$
-CONH (CH<sub>2</sub>)<sub>m</sub>  $N^{*}$ - (CH<sub>2</sub>)<sub>3</sub>SO<sub>3</sub>-

where m is 2 or 3, or variants of these in which  $-(CH_2)_3SO_3^-$  is replaced by

 $R^1$ ,  $R^2$  and  $R^3$  in these formulae are as defined previously.

Other anionic detergents beside acyl isethionate may be present notably in quantities from 10 to 50% of the

5

15

20

- 7 -

detergent mixture. Anionic detergent which is particularly envisaged is alkyl ether sulphate of the formula:

## $R^4O(CH_2CH_2O)_t$ $SO_3M$

where R<sup>4</sup> is alkyl or alkenyl of 8 to 18 carbon atoms, especially 11 to 15 carbon atoms, t has an average value of at least 2.0 and M is a solubilising cation such as sodium, potassium, ammonium or substituted ammonium. Preferably t has an average value of 3 or more.

10

15

5

Alkanolamide detergents are preferably included at only a low level, if at all, since they have been found to reduce mildness. Preferably they are restricted to not more than 5% by weight of the detergent mixture. Even better is to exclude alkanolamides and the harsh anionics, alkyl benzene sulphonate and primary alkane sulphonate completely. It is also preferred that amine oxide is not more than 5% by weight of the detergent mixture, since this has been found to reduce lather quality.

20

In particularly preferred embodiments of the present invention, the surfactant system comprises the combination of a zwitterionic detergent and one or both of an isethionate or an alkyl ether sulphate. As mentioned above, the zwitterionic detergent is preferably a betaine, be that a simple betaine, amido betaine or sulphobetaine.

- 8 -

Preferred ratios being:

- 0.05-5:1 of alkyl ether sulphate: betaine, and,
- 0.05-5:1 of cocoyl isethionate: betaine, where only a single pair of the abovementioned surfactants are present.

Where all three surfactant components are present the ratio of the total of the alkyl ether sulphate and the isetionate will generally account for 25-75% of the surfactant present.

The amount of cationic polymer is preferably at least 0.05% by weight of the whole composition. It may well not exceed 3% or even 2% of the composition.

15

20

5

10

Various cationic polymers may be used. Examples of cationic polymers include the cationic cellulose ethers described in US Patents Nos. 3816616 and 4272515 and which are available commercially from Union Carbide Corp. under the trade mark POLYMER JR. Other suitable materials are the cationic polygalactomannan gum derivatives described in US Patent No. 4298494 which are commercially available under the trade mark JAGUAR from Celanese-Stein Hall. An example of a suitable material is the

25 hydroxypropyltrimethylammonium derivative of guar gum of the formula: \_ Ç -

G-O-CH<sub>2</sub>CH-CH<sub>2</sub> N (CH)<sub>3</sub> Cl<sup>-</sup>OH

5

10

15

where G represents guar gum. Such a material is available under the name JAGUAR C-13-S. This material also has the CTFA designation Guar Hydroxypropyltrimonium Chloride. In JAGUAR C-13-S the degree of substitution of the cationic groups is about 0.13. Another possible material is that known as JAGUAR C-17 which is similar to JAGUAR C-13-S but has a higher degree of substitution of cationic groups of about 0.25-0.31. A further example of a guar derivative is the hydroxypropylated cationic guar derivative known as JAGUAR C-16 which as well as containing the above cationic quaternary ammonium groups also contain hydroxypropyl (-CH<sub>2</sub>CH(OH)CH<sub>3</sub>) substituent groups. In JAGUAR C-16 the degree of substitution of the cationic groups is 0.11-0.16 and the moles of substitution of hydroxypropyl groups is 0.8-1.1.

20

25

A surprising feature of the present invention is that stable depositing compositions can be made with both the cationic cellulose ethers (such as POLYMER JR) and the cationic polygalactomannan gums (such as JAGUAR). While JAGUAR is the more commonly used cationic polymer in the art, polymer JR is less likely to be contaminated with substances which lend a colour to the resulting compositions.

10

Other cationic polymers include cationic polyamide polymers such as the low molecular weight adipic acid/diethylene-triamine polyamide and the copolymers of vinylpyrrolidone and dimethylaminoethyl methacrylate quaternised with dimethyl sulphate (Gafquat 755, GAF Corporation) described in US Patent No. 4080310; the graft cationic copolymer containing N-vinylpyrrolidone, dimethylaminoethyl methacrylate and polyethylene glycol described in US Patent No. 4048301; the mineral acid salts of the amino-alkyl esters of homo- and copolymers of unsaturated carboxylic acids having from 3 to 5 carbon atoms described in US Patent No. 4009256; and the polymers of etherified starch described in US Patent No. 3186911.

- The high molecular weight cationic polymers are sold under the trade mark MERQUAT by Merck & Co., Inc.

  Representative ones are Merquat 100, a highly charged cationic dimethyldiallylammonium chloride homopolymer, and Merquat (TM) 550, a highly charged cationic copolymer prepared with dimethyldiallylammonium chloride and acrylamide. These materials are designated in the CTFA dictionary as Quaternium-40 and Quaternium-41, respectively.
- 25 It is preferred that the amount of silicone is at least 2% by weight of the composition and preferably at least 3% or

10

15

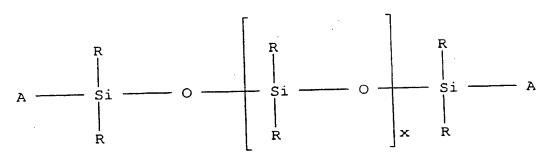
20

25

3.5%. The amount will generally not exceed 10% or even

Silicone may be an involatile silicone oil or a relatively more volatile silicone. An involatile silicone oil will generally have a viscosity of at least 5 centistokes at 25°C, e.g. 10 to 100,000 centistokes. In fact, involatile silicones are highly preferred for the invention.

Suitable silicones include polyalkyl or polyaryl siloxanes with the following structure:



wherein R is alkyl or aryl, x is an integer from about 100 to about 2,400 and A represents groups which block the ends of the silicone chains. Suitable A groups include methyl, methoxy, ethoxy, propoxy, and aryloxy. The two R groups on each silicone atom may represent the same group or different groups. Preferably the two R groups represent the same group. Suitable R groups include methyl, ethyl, propyl, phenyl, methylphenyl and phenylmethyl. The preferred silicones are polydimethyl siloxane, polydiethylsiloxane, and

30

- 12 -

polydimethylphenylsiloxane. Polydimethylsiloxane is especially preferred.

Other silicones suitable for use in the present invention include the cyclic silicones. These materials have the formula:

where n is 4 or 5 and R has the same meaning as in the structure of linear siloxanes.

The dimethyl cyclic siloxanes are volatile, and are thus present only temporarily after deposition. Volatile cyclic silicones are available under the trade name DOW CORNING 344 and 345 fluids from the Dow Corning Corporation.

20

25

5

Silicone used in this invention may well be a silicone homopolymer, although silicones may be modified by including copolymers, e.g. polyethers as is described in US Patent No. 3957970. Such copolymers tend to be more soluble than homopolymers of silicone.

Other materials may be included in compositions of this invention. Possibilities include colouring agents, opacifying agents, organic polymers, perfumes including

- 13 -

deodorant perfumes, bactericidal agents to reduce the microflora on skin, antioxidants and other preservatives.

Organic polymers which may be present include cross-linked polyacrylates such as the Carbopol (TM) polymers available from Goodrich. These can function to increase viscosity or enhance stability of a composition. Polysaccharides are also well known as thickening agents and many are cellulose or cellulose derivatives.

10

15

5

Several methods can be employed to ensure that the rod micellar phase is present. One of these is perfume, the incorporation of perfume can thereby cause an increase in viscosity. Preferably in addition, or as an alternative, the increase in viscosity can be obtained by adding inorganic electrolyte. Thickening polymers may be included as mentioned above but will generally not be required.

Where electrolyte is present the level preferably exceeds 5% wt on product and, more preferably falls into the range 5-10% on product. The preferred electrolytes are alkali

metal halides, preferably sodium chloride.

25 Compositions according to this invention are viscous emulsions with the silicone present as a disperse phase.

Such emulsions can be formed by mixing the ingredients

under conditions of high shear. However it may be preferred to introduce the silicone as a preformed emulsion so as to simplify mixing the composition.

It is preferred that the dispersed droplets of silicone oil have a mean particle size not greater than 2  $\mu m$ , preferably the mean particle size is below 1.5  $\mu m$ , most preferably in the range 0.1-1  $\mu m$ .

- 15 -

## Example 1 Detergent compositions were prepared containing:

		% by weight
5	Sodium alkyl ether sulphate	13.0
•	Cocoamidopropylbetaine	2.0
	Silicone	2.0
1	Jaguar C-13-S	0.1
	Perfume	1.0
10	Sorbic acid	0.37
	Trisodium citrate	0.37
	Sodium chloride	see below
	Water	balance to 100%

The alkyl ether sulphate was sodium lauryl ether sulphate with average 3 ethylene oxide residues per molecule, available as Genopol ZRO (TM) from Hoechst.

The cocoamidopropylbetaine was Amonyl 380BA (available from Seppic).

As mentioned above Jaguar C-13-S is a cationic guar gum derivative with the CTFA designation guar hydroxypropyltrimonium chloride, available from Celanese-Stein Hall

The silicone was added as 10% of a preformed emulsion BY22-026 from Toray Silicone Co Ltd comprising:

	Lauryl alcohol ethoxylate 2EO	2%
5	Lauryl alcohol ethoxylate 21E0	2%
	Polydimethyl siloxane (60,000 cS)	50%
	Preservative	q.s.
	Water	balance to 100%

The silicone particles in this emulsion have a mean particle size of  $0.4\mu m$ .

The compositions were made by mixing all the ingredients except sodium chloride in a paddle stirrer, and then mixing in the sodium chloride which led to an increase in viscosity of the composition.

Compositions were made containing various quantities of sodium chloride. Their viscosities were measured. The compositions were stored at 37°C and observed periodically to asses their stability. The results obtained are given below.

15

- 17 -

	Composition No.	. 1	2	3
	wt% NaCl	1.95	2.30	3.00
	Viscosity (Pa.sec) at 25°C, 10 sec	4.8	7.5	11.0
5	Storage at 20°C for 3 months	stable	stable	stable
10	Storage at 37°C for 3 months	slight separation of silicone	stable	stable

Portions of the compositions were subjected to freeze-thaw cycling, alternating 12 hours at -10°C with and 12 hours at 20°C. After 6 cycles none of the compositions showed any instability.

5

## Example 2

A number of compositions were prepared, with ingredients as set out in the following table. They were tested for stability by storing for 6 to 12 months at 25°C. None showed any instability.

		1	2	3	4	5	6
	Ingredient						
	Sodium lauryl ether sulphate 3EO	12	12	12	12	12	12
10	Cocobetaine	3	3	-3	. 3	3	3 ·
	NaCl	1.5	1.5	1.5	1.5	1.5	1.5
15	Jaguar C-13-S	0.1	0	0.25	0	0.05	. 0
	Polymer JR400	0	0.1	0	0.25	0	0.05
	Silicone (BY22-026)	5	5	5	5	5	5 , .
20	Perfume	1	1	1	1	1	1
	Formalin	0.1	0.1	0.1	0.1	0.1	0.1
25	Water		ba	alance	e to 1	L00% .	
·	Viscosity (Pa. sec at 10 sec )	10.9	5 10.5	5 10.2	2 10.0	9.5	10.0

The coconut betaine was of formula:

30 R<sup>1</sup>CO-N<sup>+</sup>-CH<sub>2</sub>CO<sub>2</sub>-CH<sub>3</sub>

> in which R¹CO- is a mixture of acyl groups derived from coconut. This betaine was Empigen (Registered Trade Mark) BB from Albright and Wilson.

35

- 19 -

The silicone oil was added as 10% of the preformed BY22-026 Emulsion from Toray Silicone Co Ltd.

- 20 -

### Example 3

In this Example and those which follow, a number of tests were carried out by human volunteers. The experimental procedure employed was as follows:

5

10

The volunteer washed one forearm with a control shower gel containing neither silicone nor cationic polymer. This was carried out by wetting the arm and also the volunteer's free hand with warm water then using the free hand to lather the arm with 0.5 grams of the control shower gel, next rinsing for 10 seconds while rubbing with the free hand and then drying the arm with a paper towel.

After this pre-washing the volunteer washes the same

forearm with a test product using the same procedure.

When drying the forearm care is taken that the paper towel is drawn only once across a test area of the forearm.

a strip of adhesive tape onto the area keeping it in place for 30 seconds using a spring loaded device bearing on a rubber bung to press the tape onto the skin with a repeatable pressure of 85g.cm<sup>-2</sup>. The adhesive tape employed was J-Lar Superclear (TM) tape having a width of

25 25mm.

10

5 or more such strips of tape are applied in this way one after another to the same area of skin.

In this test procedure silicone which has deposited on the skin will subsequently be transferred to the tape along with some of the outer layer of the volunteer's skin.

The amounts of silicone and skin adhering to the tape are determined by means of X-ray fluorescence spectroscopy. The tape strips are placed in an X-ray fluorescence spectrometer with the adhesive side facing the beam of this machine. A mask is applied over the tape to define a standardised area in the middle of the tape which is exposed to the X-ray beam. The sample chamber of the machine is placed under vacuum before making measurements and the spectrometer is then used to measure the quantities of silicone and sulphur. The sulphur is representative of the amount of skin which has transferred to the tape.

20

15

The amounts of silicone and sulphur observed with a clean piece of adhesive tape are subtracted from the experimental measurements. The experimental measurements for successive pieces of tape are added together and the cumulative totals of silicone and sulphur are expressed as a ratio of silicone to sulphur.

WO 94/03152 PCT/EP93/02072

- 22 -

A shower gel contained the following:

		% by weight
	Sodium cocoyl isethionate	9.0
5	Coconut betaine	6.0
	Silicone oil	5.0
	Jaguar C-13-S	0.1
	Formalin	0.1
	Water	balance to 100%

10

20

The sodium cocoyl isethionate was Fenopon (Registered Trade Mark) AC78 available from GAF Corporation. The coconut betaine was of Empigen.

The silicone was again added as 10% of the preformed emulsion BY22-026 from Toray Silicone Co Ltd.

The shower gel composition was made by mixing all the ingredients in a paddle stirrer. This led to an increase in viscosity of the mixture. After mixing the viscosity of the composition it was measured as  $15.0 \, \text{Pa.S}$  at  $10 \, \text{sec}^{-1}$ .

Silicone deposition by this composition was measured by

the test-procedure described above. It was compared with

silicone deposition from an identical composition

omitting the Jaguar C-13-S.

- 23 -

The cumulative results from 8 test strips were:

•	Total Si	Total S	Si/S Ratio
with Jaguar	2.8	4.7	0.60
without Jaguar	0.4	4.4	0.09

- 24 -

#### Example 4

A shower gel contained the following:

		% by weight
5	Sodium cocoyl isethionate	5.0
	Coconut amidopropyl betaine	8.0
	Sodium lauryl ether sulphate 3EO	2.0
	Silicone oil	5.0
	Jaguar C-13-S	0.1
10	Formalin	0.1
	Perfume	1.0
	Water	balance to 100%

The coconut isethionate was Fenopon AC78 as in the previous Example.

The coconut amidopropyl betaine was of the formula:

$$CH_3$$
|
 $R^1CONH(CH_2)_3$   $N^*$   $-CH_2CO_2$ 
|
 $CH_3$ 

in which R<sup>1</sup>CO- is a mixture of acyl groups derived from coconut. This was Rewoteric AMB 14 (TM) from Rewo.

The sodium lauryl ether sulphate was Empicol 0251 from Albright and Wilson.

The silicone was again BY22-026 emulsion.

15.

20

25

Again the shower gel was made by mixing the ingredients, with the salt added last. Viscosity of the composition was measured as 15,000 centipoise at  $10 \, \text{sec}^{-1}$ .

5 Silicone deposition was measured by the procedure described, and compared with that from an identical composition without the Jaguar C-13-S. The cumulative results from 8 test strips were:

10	Total Si		Total S	Si/S Ratio
	with Jaguar	2.0	4.9	0.41
	without Jaguar	0.6	5.2	0.12

## Example 5

The silicone deposition from compositions 1 and 2 of Example 2 was tested by the procedure given in Example 3 and compared with deposition from a similar composition without polymer. The cumulative results obtained from 7 test strips were:

		Total Si	Total S	Si/S Ratio
	with Jaguar	3.7	4.4	0.84
10	with JR400	4.2	5.3	0.79
	without Jaguar	0.6	4.2	0.14

10

15

20

#### CLAIMS:

A detergent composition in the form of an aqueous liquid or gel, a substantial part of which is in the rodmicellar phase, containing:

5 to 50% by weight of non-soap detergent,

0.01 to 5% by weight of cationic polymer, and

0.5 to 15% by weight of silicone,

where the detergent composition has a viscosity of at least 6,000 centipoise at a hear rate of 10 sec<sup>-1</sup>.

- A composition according to claim 1 wherein the detergent comprises 30 to 100% by weight, based on the total detergent, of anionic detergent.
- A composition according to claim 1 or claim 2 wherein 3. the detergent comprises 20 to 50% by weight, based on the total detergent, of a zwitterionic detergent which has a hydrophilic head group containing both a quaternary nitrogen atom and at least one acid group.
  - A composition according to claim 3 wherein the zwitterionic detergent is of the general formula:

25
$$R^{1} - \left[-C - NH \left(CH_{2}\right)_{m} - \right] - N^{*} - X - Y$$

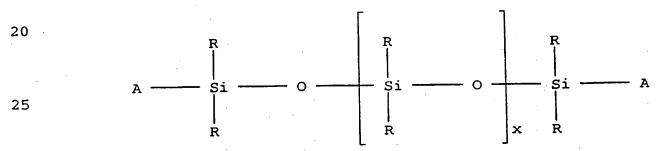
$$R^{3}$$

where  $R^1$  is alkyl of alkenyl of 7 to 18 carbon atoms  $R^2$  and  $R^3$  are each independently alkyl, hydroxyalkyl or carboxyalkyl of 1 to 3 carbon atoms

m is 2 to 4

n is 0 or 1.

- 5. A composition according to any one of the preceding claims containing 0.05% to 2% by weight of cationic, polymer.
- 6. A composition according to any one of the preceding claims wherein the cationic polymer is selected from the group consisting of cationic cellulose ethers and cationic polygalactomannan gums.
- 7. A composition according to any one of the preceding claims wherein the silicone is a polysiloxane with the structure:



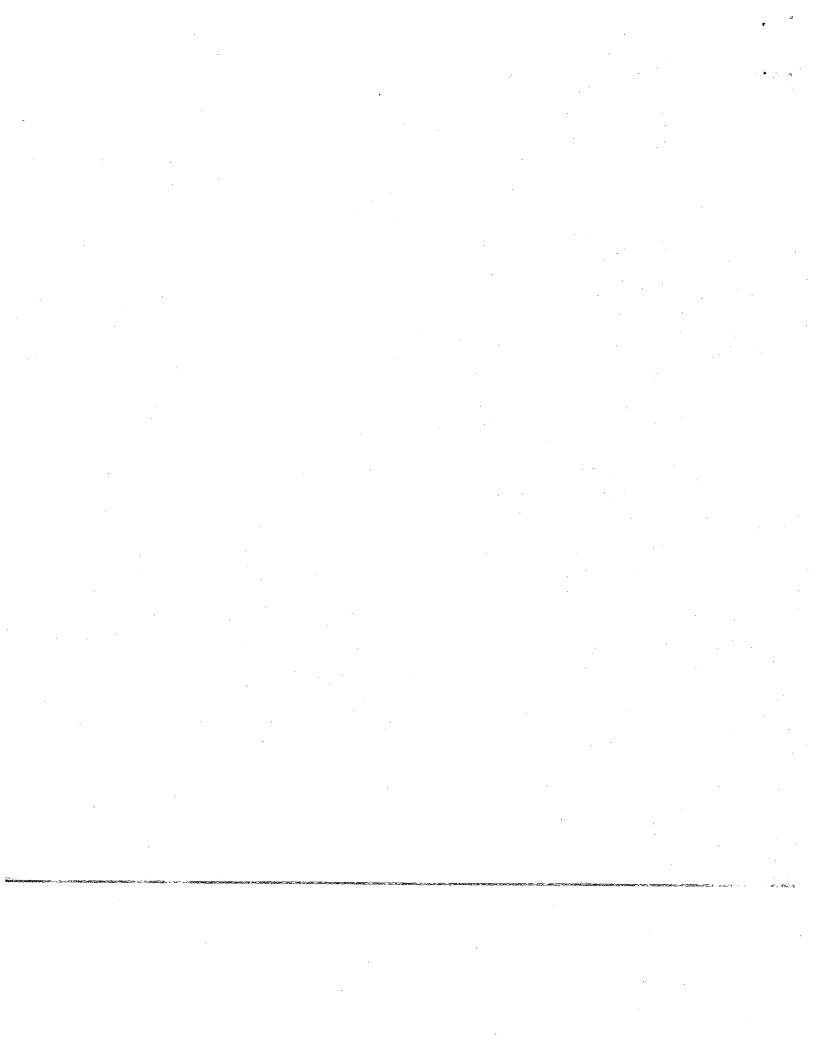
wherein R is alkyl or aryl, x is an integer from about 100 to about 2,400 and A represents groups which block the ends of the silicone chains.

8. A composition according to any one of the preceding claims containing 2% to 8% by weight of silicone.

- 9. A composition according to claim 8 containing 3.5 to 8% by weight of silicone oil.
- 10. A composition according to any one of the preceding claims wherein the silicone oil has a viscosity of at least 5 centistokes at 25°C.
  - 11. A composition according to any one of the preceding claims which also contains inorganic electrolyte.
  - 12. A composition according to any one of the preceding claims which does not include more than 0.5% by weight of esters or alcohols having two alkyl or acyl groups with more than 20 carbon atoms in total, nor more than 0.5% by weight of Scleroglucan gum.
  - 13. A composition according to any one of the preceding claims wherein the silicone oil is dispersed as droplets with particle size no larger than 2.0 $\mu m$ .

5

10



## WORLD INTELLECTUAL PROPERTY ORGANIZATION



#### INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5:		(11) International Publication Number:	WO 94/03152
A61K 7/48, 7/50, 7/06	A3	(43) International Publication Date:	17 February 1994 (17.02.94)

PCT/EP93/02072 (21) International Application Number: (74) Agent: ELLIOTT, Peter, William; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44

(22) International Filing Date: 3 August 1993 (03.08.93) ILQ (GB).

(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). 9216758.4 7 August 1992 (07.08.92) GB (71) Applicant (for AU BB CA GB IE LK MN MW NZ SD only):

UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).

(71) Applicant (for all designated States except AU BB CA GB IE LK MN MW NZ SD): UNILEVER NV [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).

(72) Inventor: HELLIWELL, John, Fielden; 9 Crossley Drive, Heswall, Wirral, Merseyside L60 9JA (GB).

**Published** 

With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(88) Date of publication of the international search report: 31 March 1994 (31.03.94)

(54) Title: DETERGENT COMPOSITION

(57) Abstract

(30) Priority data:

The invention relates to detergent compositions in liquid or gel form. The compositions comprise 5-50 %wt by weight of a non-soap detergent, which is preferably a mixture of a betaine and at least one of SLES and isctionate, 0.01-15 %wt of a cationic polymer and 0.5-15 % of a silicone. The compositions are characterised by a rod-micellar structure which provides a viscosity of at least 6000 centipoise at a shear rate of 10/sec. This rod-micellar structure can be generated by the presence of electrolyte or perfume in the compositions.

## FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	MR	Mauritania
AU	Australia	GA	Gabon	MW	Malawi .
BB	Barbados	GB	United Kingdom	NL	Netherlands
BE	Belgium	GN	Guinea .	NO.	Norway
BF	Burkina Faso	GR	Greece	NZ	New Zealand
BG	Bulgaria	HU	Hungary	PL	Poland
BJ	Benin	1E	Ireland	PT ·	Portugal
BR	Brazil	ιT	Italy	RO	Romania
CA	Canada	JP	Japan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic	SD	Sudan
CC	('ongo		of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SK	Słovak Republic
Cl	Côte d'Ivoire	: к2	Kazakhstan	SN .	Senegal
CN1	Cameroon	1.1	Liechtenstein	SU	Soviet Union
cs	Czechoslovakia -	LK	Sri Lanka	TD:	Chad
C2	Czech Republic	1.0	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	UA	Ukraine
DK	Denmark	MC	Madagascar	US	United States of America
ES	Spain	Ml.	Mali	VN	Viet Nam
FI	Finland	MN	Mongolia		
			•		

#### INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 93/02072 A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 A61K7/48 A61K7/ A61K7/50 A61K7/06 According to International Patent Classification (IPC) or to both national classification and IPC **B. FIELDS SEARCHED** Minimum documentation searched (classification system followed by classification symbols) IPC 5 A61K Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) C. DOCUMENTS CONSIDERED TO BE RELEVANT Relevant to claim No. Category Citation of document, with indication, where appropriate, of the relevant passages 1-13 EP,A,O 468 721 (UNILEVER PLC) 29 January X see the whole document 1-9,13X EP, A, O 432 951 (UNILEVER PLC) 19 June 1991 cited in the application see the whole document EP,A,O 400 976 (UNILEVER PLC) 5 December 1-10 X 1990 see the whole document X GB,A,2 236 321 (KAO CORPORATION) 3 April 1,2, 5-10,12 1991 see the whole document Further documents are listed in the continuation of box C. Patent family members are listed in annex. Special categories of cited documents: "I later document published after the international filing date or priority date and not in conflict with the application but "A" document defining the general state of the art which is not considered to be of particular relevance cited to understand the principle or theory underlying the invention earlier document but published on or after the international "X" document of particular relevance; the claimed invention filing date cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another document of particular relevance; the claimed invention citation or other special reason (as specified) cannot be considered to involve an inventive step when the document referring to an oral disclosure, use, exhibition or document is combined with one or more other such do ments, such combination being obvious to a person skilled other means document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report the statute of the maintenance of the control 15,02.94 2 February 1994 Name and mailing address of the ISA Authorized officer

Form PCT/ISA/210 (second sheet) (July 1992)

Fax (+31-70) 340-3016

European Patent Office, P.B. 5818 Patentiaan 2 NL - 2280 HV Rijswijk Td. (+ 31-70) 340-2040, Tx. 31 651 epo nl,

Sierra Gonzalez, M

## INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 93/02072

ategory *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	EP,A,O 463 780 (UNILEVER PLC) 2 January 1992	1-9
	see the whole document	1
,		
	·	
·		
		·

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

## INTERNATIONAL SEARCH REPORT

Information on patent family inembers

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0468721	29-01-92	AU-B- 639351 AU-A- 8118291 CA-A- 2047105 GB-A- 2246575 JP-A- 4234309 US-A- 5246694	22-07-93 30-01-92 24-01-92 05-02-92 24-08-92 21-09-93
EP-A-0432951	19-06-91	AU-B- 620746 AU-A- 6772590 DE-D- 69004057 JP-A- 4364111 JP-A- 4036226	20-02-92 06-06-91 25-11-93 16-12-92 06-02-92
EP-A-0400976	05-12-90	AU-B- 624514 AU-A- 5606690 JP-A- 3068509 JP-B- 4000964 US-A- 5152914	11-06-92 06-12-90 25-03-91 09-01-92 06-10-92
GB-A-2236321	03-04-91	JP-A- 3115498	16-05-91
EP-A-0463780	02-01-92	GB-A- 2245279 AU-B- 636231 AU-A- 7846091 JP-A- 4243812	02-01-92 22-04-93 02-01-92 31-08-92

Form PCT/ISA/210 (patent family annex) (July 1992)

